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VI. "Researches on the Phosphorus-Bases." By A. W. HORMANN, Ph.D., F.R.S. &c. Received May 28, 1858.

In a paper published in the Transactions of the Royal Society, we (M. Cahours and myself) have given a detailed account of the preparation of the phosphorus-bases, and also an accurate description of triethylphosphine, the most characteristic and accessible representative of this class of compounds.

The object of our joint inquiry was chiefly to examine the phosphorus-bases as a class, and to establish their analogy with the corresponding terms of the nitrogen-series. The deportment of the phosphorus-bodies in their relation to other compounds has as yet been scarcely investigated. For several months I have been engaged in this study, which promises a rich harvest of results. Most of the experiments were made with triethylphosphine, a substance which, in consequence of its convenient position in the system of organic compounds, in consequence of the variety of its attachments, the energy and precision of its action, and, lastly, the well-defined character of its compounds, will probably become an agent of predilection in the hands of the chemist.

It is my intention to trace the history of this remarkable body in its several directions; and for this purpose, in fact, a considerable amount of material has been already accumulated. But since necessarily some time must elapse before such an inquiry, which from the peculiar character of the compound is often obstructed by unusual difficulties, can be completed, I beg leave to present my results in the same measure as the inquiry advances, hoping that at a later period I may be allowed to collect the scattered observations, and to lay them in a more elaborated and digested form before the Society.

Among the numerous reactions of triethylphosphine, my attention has been chiefly directed to the compounds which this body furnishes when submitted to the action of organic chlorides, bromides, and iodides.

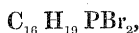
I. *Action of Bibromide of Ethylene upon Triethylphosphine.*

In the anhydrous condition the two bodies act even at the common temperature with considerable power upon each other, a white cry-

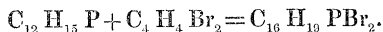
stalline substance being immediately precipitated. If the reaction be allowed to go on in the presence of a large volume of anhydrous ether, the deposition of the crystalline body is considerably retarded, unless the mixture, in an appropriate apparatus, be exposed to the temperature of boiling water. After a short digestion, on distilling off the ether and the excess of bibromide, a crystalline cake is left in the retort, consisting of several bromides, the nature and the relative proportions of which appear in a great measure to depend upon the rapidity of the reaction. I have found it most convenient to work with ethereal solutions at the common temperature.

The determination of the bromine in the crystalline body revealed at once the compound character of this substance, for it steadily diminished by dissolving the bromide in absolute alcohol, and reprecipitating it partially by ether. By repeating this process four or five times, a body of constant composition was obtained.

The compound thus prepared is a crystalline mass, without odour, extremely soluble in water, and even in absolute alcohol, but insoluble in anhydrous ether. It exhibited a rather unexpected composition, for on analysis it was found to contain



and consequently to have been formed by the simple union of 1 equivalent of triethylphosphine and 1 equivalent of bibromide of ethylene,



The bromine in this compound exists in two perfectly different forms; addition of nitrate of silver precipitated only one-half of this element as bromide of silver, while even by protracted ebullition the second half remained untouched. The result changed, however, on digestion with freshly precipitated oxide of silver, when the whole of the bromine separated at once in the form of bromide of silver.

On adding to the solution of the bromide an excess of nitrate of silver, filtering off the bromide, and removing the excess of silver by hydrochloric acid, a corresponding chloride was obtained, from which bichloride of platinum precipitated a beautiful orange-yellow platinum-salt. In a moderately diluted solution which had been previously gently heated, no immediate precipitate was produced; but on cooling, the same salt was deposited in magnificent needles, which

could be recrystallized from boiling water, or better from hydrochloric acid.

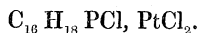
This compound contained



A difficultly soluble gold-salt, crystallizing from boiling water in small scales, was found to have the corresponding composition,



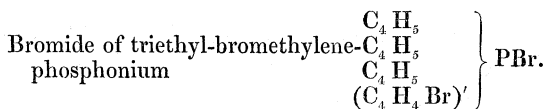
Very different results were observed when the whole of the bromine was removed by means of oxide of silver. A powerfully alkaline solution was thus obtained, which, converted into hydrochlorate, gave, with bichloride of platinum, a precipitate only after very considerable evaporation. The precipitate was likewise of a deep orange-red colour; it readily dissolved in boiling water, from which it separated on cooling in the form of well-defined octahedra having the composition



Tetrachloride of gold furnished likewise a crystalline precipitate very similar in appearance to the gold-salt previously mentioned, but containing

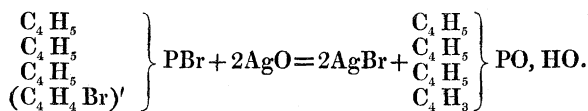


The action of dibromide of ethylene on triethylphosphine, and the subsequent transformation of the compound produced, is readily explained. The two substances unite in equal equivalents, the product of the reaction being the bromide of a phosphonium, in which the fourth equivalent of hydrogen is replaced by a compound molecule, $\text{C}_4\text{H}_4\text{Br}$ (brominated ethyl?), of monatomic substitution-power,



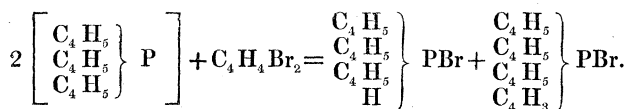
The compound phosphonium of this bromide possesses very considerable stability, as is sufficiently evinced by its deportment with nitrate of silver, and by the formation of the platinum- and of the gold-salt. All my attempts, however, to separate the base itself have entirely failed. Under the influence of oxide of silver, the bromide yields an alkaline solution possessing all the characters of the -onium-bases. The body in solution, however, no longer belongs

to the same series, the elements of hydrobromic acid having separated from the original compound metal.



The compound thus obtained may be designated as the hydrated oxide of triethyl-vinyl-phosphonium.

I have ascertained by experiment that the brominetted bromide is by no means the only result of the action of bibromide of ethylene on triethylphosphine, although under favourable circumstances it appears to be the chief product. Invariably a portion of the bibromide, faithful to its traditions, splits into hydrobromic acid and bromide of vinyl; and we find therefore in the white crystalline mass always, together with hydrobromate of triethylphosphine, a certain quantity of the very bromide of triethyl-vinyl-phosphonium, which, as has been stated, results from the action of oxide of silver on the brominetted bromide.



The action of bibromide of ethylene on triethylphosphine, complex as it is, receives an additional element of complication by the influence of heat. Ebullition appears to facilitate the formation of a fourth bromide, which, although less prominently, is also produced in the cold. The study of this compound is not yet completed.

VII. "Researches on the Phosphorus-Bases."—No. II. Action of Bisulphide of Carbon on Triethylphosphine. By A. W. HOFMANN, Ph.D., F.R.S. &c. Received June 5, 1858.

Among the many characteristic reactions of the phosphorus-bases, their deportment with sulphur is so conspicuous that it has served frequently as a test for the presence of these substances. In continuing the study of the phosphorus-bases, I have found that this remarkable attraction for sulphur is by no means limited to this element in the free state. Many sulphur-compounds, when coming